Resin in Bisulfite Pulp From Pinus radiata Wood and Its Relationship to Pitch Troubles

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PROBLEMS are caused by accumulation of pitch deposits during production of paper from unbleached *P. radiata* bisulfite pulp. The literature prior to 1962 has been reviewed by Cohen (*1*). The resin in sulfite pulps from *Picea abies* wood has been extensively studied whereas less is known about that in bisulfite pulps from *Pinus* species. The quantity of resin removed at different stages of pulp manufacture varies considerably (*2–7*). Resin undergoes significant changes during pulping (*8*), and some components are selectively removed during washing of the pulp (*2, 9*). Several factors affecting the resin content of sulfite pulp are not well defined. In some instances conflicting results have been reported. There have been no published reports of the composition of pitch deposits found in paper mills.

To understand these problems, we have determined the resin content of bisulfite pulp at various stages in its manufacture and observed the concurrent changes in the composition of the resin. Chemical analyses were carried out on pitch which accumulated on pulp processing equipment and paper machines.

RESULTS AND DISCUSSION

Resin in Chips and Pulps

Change in Total Resin Content. The resin content of *P. radiata* wood chips and a number of bisulfite pulps prepared from this species are shown in Table I. The average resin content of three additional chip samples was 2.0%, which was in reasonable agreement with that for the chips used in the basket cook. As the pulp yield was 50%, about half of the resin present in the wood was lost during the bisulfite cook. Diffusion washing of pulp in the blowpits removed an additional 11% and screening a further 8%.

The spent liquor contained 0.15% ether-soluble material. The resin acid fraction was 40% of the ether solubles but it was not possible to estimate the amount of fatty acids present because of the complexity of the mixture. The two main components, eugenol and *trans-iso*-eugenol, are degradation products of lignin (*10*) and comprised 30% of the total material. At the end of a cook the

Abstract: The resin content of bisulfite pulp from *Pinus radiata* D. Don was determined at various stages in its manufacture and the changes in the composition of the resin studied. About 50% of the resin present in the wood was removed during cooking, an additional 11% by blowpit washing, and a further 8% by screening. Resin acids and fatty acids were preferentially lost during washing and screening of the pulp, whereas the amount of fatty acid esters in the pulp was not significantly reduced. There was no selective loss of individual resin acids and fatty acids during washing and screening of the pulp. Pitch deposits from the pulp mill and paper machine were mixtures of resin and acetone-insoluble material, and the trouble caused by a deposit was related to its viscosity. The resin in these deposits contained about 50% acidic compounds. The fatty acid and unsaponifiable fractions showed the greatest tendency to accumulate in pitch deposits.

Keywords: Resin acids · Fatty acids · Esters · Bisulfite pulping · Washing · Screening · Chemical analysis · Pitch (material) · Viscosity · Dihydroabietic acid*

stock concentration was 15% and the volume of liquor corresponding to 100 g of pulp would contain 1% ether-solubles. After allowing for the phenolic fraction (0.3%) the maximum amount of resin that could be present would be 0.7%. This leaves a discrepancy amounting to 30% of the resin present in the wood. The most likely explanation would be that during cooking some of the resin is converted into ether-insoluble material. Similarly, Malevskaya and Litvinova (*4*) studying pine sulfite pulping could not account for 15–55% of the original wood resin.

An increase in the temperature of the water used for diffusion washing of pulp in the blowpits did not reduce the resin content of the washed pulp (Table I). When the pulp is discharged from the digester into the blowpits, the lower portion of the pulp mass is tightly packed over the filter plates and acts as a fine

mesh filter. It would be difficult for a suspension of resin particles to pass through the pulp mass. Resin is almost insoluble in water, and increasing the water temperature would not appreciably increase its solubility.

The efficiency of the screening process for resin removal is underestimated in this study. The machine wire functioned as a screen and allowed short fibers and resin-containing ray cells to pass through it (*11*). This pulp was recovered with a save-all consisting of a drum filter and its resin content was higher than that of screened pulp (Table I). As the save-all pulp was added to the washed pulp immediately before the screening stage, the resin content of the pulp entering the screen would be higher than that of washed pulp.

Change in Resin Composition. The amounts of different classes of resin components per 100 g of pulp are shown

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Table I — Amount and Composition of Resin in Chips and Pulps

Sample	Resin in sample, %	Method of analysis	Composition of resin, %			
			Resin acids	Fatty acids	Esterified fatty acids	Unsaponifiables
Basket Cook						
Uncooked chips	1.60	B	61	4	23	12
Cooked chips	1.47	A	57	11	24	8
145°F Washing						
Unwashed pulp	1.48	A	63	11	17	9
Washed pulp	1.13	B	60	8	21	11
Screened pulp	0.88	B	49	5	35	11
200°F Washing						
Unwashed pulp	1.34	A	57	10	20	13
Washed pulp	1.14	B	55	7	27	11
Screened pulp	0.84	B	42	6	39	13
Save-all pulp	0.95	A	15	5	55	25

in Table II. About 80% of the resin acids, 60% of the fatty acids, 57% of the esterified fatty acids, and 71% of the unsaponifiables present in the wood chips were removed during pulping and subsequent washing and screening of the pulp. During the cooking process there was a considerable loss of resin acids, esterified fatty acids, and unsaponifiables, but a slight increase in the fatty acid fraction because of hydrolysis of fatty acid esters. The principal components lost during washing and screening of the pulp were resin acids and fatty acids. The amount of esterified fatty acids was unchanged by washing but increased after screening because of the introduction of save-all pulp and the failure of screening to effectively remove ray parenchyma cells (11).

In conifers the resin canals and adjoining epithelial cells contain mainly resin acids, whereas ray parenchyma cells contain principally esterified fatty acids (12). During the cooking process the resin acids are released and would be a major component of the resin on the outside of fibers and suspended in the water. The parenchyma resin is retained within the cells as long as these are not damaged by mechanical or chemical treatment. The preferential removal of resin acids by washing and screening is a result of their greater accessibility. The esterified fatty acids can only be lost by removal of intact ray parenchyma cells or by rupture of the cells. This would not occur to a large extent during blowpit washing of pulp. The large proportion of esterified fatty acids in save-all pulp is consistent with its high content of ray parenchyma cells.

Change in Individual Resin Components. The proportions of individual resin acids in the resin acid fractions are shown in Table III. The composition of the resin acids in wood chips is similar to that found in other studies of *P. radiata* resins (13–15). The lower content of levopimaric + palustric and neoabietic acids and the increase in dehydroabietic acid was probably the result of oxidation and isomerization which occurred during storage of the wood (16). The change in resin acid composition was the result of the well-known instability of the abietic-type resin acids towards acids and heat (17, 18). The principal resin acids in unwashed pulp and spent liquor were abietic and dehydroabietic acids. The effect of the cooking conditions on the pimaric group of acids was very small. Washing and screening of the pulp did not appreciably alter the composition of the resin acids.

The composition of the fatty acid and esterified fatty acid fractions from chips and pulps is shown in Table IV. There is very little selectivity in the changes in the amounts of free fatty acids and esterified fatty acids during pulping and subsequent washing and screening of the

pulp. A similar result was reported by Swan (9) in a study of spruce pulp. The greatest changes were the larger proportions of palmitic acid and esterified arachidic acid in save-all pulp.

Pitch

Composition of Pitch Deposits. Analyses of pitch deposited in the pulp mill and on various parts of the paper machine are shown in Table V. The deposits contained large proportions of material insoluble in acetone, and in one instance this comprised about 70% of the sample. A similar result was reported by Affleck and Ryan (19), who examined pitch from a kraft mill. Many studies on pitch do not emphasize this affinity of resins

for solids. In the pulp mill the acetone-insoluble fraction of the pitch deposits consisted of sand, small stones, and fiber, whereas those formed in the paper machine and its associated systems contained talc, asbestos, water-insoluble metal salts, fiber, and in some cases, dyes. Oil-soluble dyes were particularly susceptible to inclusion. Sample 6 contained much less acetone-insoluble material than the others and was particularly sticky. The viscosity and tackiness of pitch is influenced by the insoluble material, and it is converted to a relatively harmless form when the amount is increased. Finely divided minerals, such as asbestos and talc, are widely used for pitch control, and this would be the reason for their success.

Table II. Weight (grams) of Resin Components per 100 g of Pulp

Sample	Resin acids	Fatty acids	Esterified fatty acids	Unsaponifiables
Wood chips[a]	1.95	0.13	0.74	0.38
Spent liquor[b]	0.30	ND[c]	ND[c]	ND[c]
Unwashed pulp[d]	0.82	0.15	0.26	0.15
Washed pulp[d]	0.66	0.09	0.28	0.13
Screened pulp[d]	0.39	0.05	0.32	0.11
Save-all pulp	0.14	0.05	0.52	0.24

[a] Quantities doubled to take into account a pulp yield of 50%.
[b] Amount present in liquor corresponding to 100 g pulp.
[c] Not determined.
[d] Average of 145 and 200°F washings.

Table III. Composition of Resin Acid Fraction From Chips, Spent Liquor, and Pulps

Sample	Percentage of total resin acid peak area[a]						
	Pim	San	Levo/Pal	Iso	Abie	Dehyd	Neo
Uncooked chips	9.6	1.6	42	2.5	11	20	13
Cooked chips	6.0	1.6	9.9	3.4	55	19	4.2
Spent liquor	3.7	1.4	5.8	4.9	50	33	1.7
Unwashed pulp	5.3	1.4	10	3.8	52	23	4.3
Washed pulp	6.9	1.9	13	2.5	57	12	6.8
Screened pulp	6.1	1.9	13	3.9	57	13	5.3
Save-all pulp	5.9	1.1	11	4.0	61	13	4.2

[a] Pim = pimaric, San = sandracopimaric, Levo/Pal = levopimaric + palustric, Iso = isopimaric, Abie = abietic, Dehyd = dehydroabietic, and Neo = neoabietic acid.

Table IV. Composition of Fatty Acid and Saponifiable Fatty Acid Fractions From Chips and Pulps

Sample	Percentage of total fatty acid peak area[a]					
	C_{16}	C_{18}	C_{18}^1	C_{18}^2	C_{18}^3	C_{20}
Uncooked chips						
Free	12	2.0	63	21	—	2.0
Esterified	9.1	1.3	54	31	1.7	2.7
Cooked chips						
Free	13	2.0	48	30	3.3	3.2
Esterified	9.3	1.0	48	36	2.9	3.2
Unwashed pulp						
Free	11	2.1	54	27	2.4	3.3
Esterified	13	1.3	46	34	3.2	3.0
Washed pulp						
Free	14	2.6	57	23	1.6	1.5
Esterified	11	2.3	45	38	1.3	3.1
Screened pulp						
Free	13	4.0	61	19	1.4	1.9
Esterified	11	2.6	47	35	2.2	2.0
Save-all pulp						
Free	21	2.1	51	22	2.9	1.0
Esterified	7.8	0.8	45	35	3.3	8.3

[a] C_{16} = palmitic, C_{18} = stearic, C_{18}^1 = oleic, C_{18}^2 = linoleic, C_{18}^3 = linolenic, and C_{20} = arachidic acid.

Composition of Resin from Pitch.

The acetone-soluble portions were separated into four fractions—resin acids, fatty acids, esterified fatty acids, and unsaponifiables (Table V). In general the pitch deposits in the pulp mill contained higher percentages of resin acids than those deposited during papermaking, the exception being sample 7. All pitch samples contained larger proportions of fatty acids but lower amounts of esterified fatty acids than the resin in pulp. A particularly interesting aspect was the large quantity of unsaponifiable material. Pitch deposited on the machine chest and broke chest walls contained appreciable quantities of betulin from bleached birch kraft pulp used in the manufacture of one of the products.

Studies have been carried out to determine the resin components responsible for pitch formation (5, 20). Starostenko and co-workers (21) showed that resin would have little tack and a low pitch-causing potential when its resin acid content was lower than 25% or greater than 75%. Back (22) claimed that the viscosity of the resin was one of the important factors influencing its accumulation at solid surfaces. Our results are difficult to correlate with previous work because of the presence of the acetone-insoluble material, but there is a relationship between the viscosity of the pitch and the trouble it caused. The least troublesome pitch deposit (sample 3) contained 19% resin acids, and this is below the minimum of 25% mentioned by Starostenko (21).

Amounts of Individual Resin Components. The compositions of the resin acid fractions from the pitch samples are shown in Table VI. Four of the samples contained an acid which was not present in wood chips, spent liquor, or any of the pulps. Mass spectrometry, NMR spectroscopy, and a comparison of the GLC retention time of the methyl ester with those of the known dihydroabietic acids suggested it was most likely to be 8-β-abiet-13-ene-18-oic acid.

There was a correlation between the amount of dihydroabietic acid in the pitch deposit and the probable age of the deposit. Pitch in the centrifugal pulp cleaner was removed every few days and did not contain any dihydroabietic acid. The pitch deposit from the pulp storage tower, which is cleaned annually, contained a large amount. The most likely explanation for the formation of dihydroabietic acid is disproportionation of abietic-type resin acids. This is supported to some extent by the inverse relationship of the amounts of dihydroabietic and abietic acids. The disproportionation may take place over long periods of time at room temperature in the presence of traces of acid.

The composition of the fatty acid and saponifiable fatty acid fractions from the pitch deposits are shown in Table VII. In the fatty acid fractions the predominant acid was oleic acid, whereas linoleic acid was the major component in most esterified fatty acid fractions. The fatty acid and esterified fatty acid fractions from the wood chips and pulps (Table IV) all had higher proportions of oleic acid. The esters of linoleic acid may undergo hydrolysis more slowly than those of oleic acid. Consequently a greater proportion of linoleic acid esters accumulate in the esterified fatty acid fractions in many of the pitch deposits. The esterified fatty acid fractions from the two pitch samples which did not have a predominance of linoleic acid esters contained high proportions of palmitic acid esters.

Table V. Composition of Pitch Deposits

Source of deposit	Percentage soluble in acetone	Percentage composition of soluble material			
		Resin acids	Fatty acids	Esterified fatty acids	Unsaponifiables
1. Centrifugal cleaner	23	46	19	14	20
2. Pulp storage tower	45	57	18	8	17
3. Machine chest wall	36	19	14	12	53 (13% betulin)
4. Broke chest wall	37	35	14	11	40 (8% betulin)
5. Machine wire water pit	57	30	12	14	44
6. Felt water pit	77	32	14	4	50
7. Backwater race for feltwater	34	57	12	10	21

Table VI. Composition of Resin Acid Fraction From Pitch Deposits

Source of deposit	Percentage of total resin acid GLC peak area[a]							
	Pim	Dihyd	San	Levo/Pal	Iso	Abie	Dehyd	Neo
1. Centrifugal cleaner	6.2	...	2.5	8.0	6.1	60	16	1.4
2. Pulp storage tower	4.3	14	1.4	7.0	5.4	48	18	2.2
3. Machine chest wall	10	...	3.4	10	10	47	17	1.9
4. Broke chest wall	10	27	NM[b]	4.3	8.7	31	19	...
5. Machine wire water pit	10	...	2.1	14	7.9	54	6.7	5.2
6. Felt water pit	7.4	0.4	2.0	8.7	6.2	67	5.9	2.6
7. Backwater race for feltwater	8.1	19	0.8	13	6.5	32	16	4.5

[a] Pim = pimaric, Dihyd = dihydroabietic, San = sandracopimaric, Levo/Pal = levopimaric + palustric, Iso = isopimaric, Abie = abietic, Dehyd = dehydroabietic, and Neo = neoabietic acid.
[b] Not measurable.

Table VII. Composition of Fatty Acid and Saponifiable Fatty Acid Fractions From Pitch Deposits

Source of deposit	Percentage of total fatty acid GLC peak area[a]					
	C_{16}	C_{18}	C_{18}^1	C_{18}^2	C_{18}^3	C_{20}
1. Centrifugal cleaner						
Free	3.3	0.5	55	32	4.6	4.3
Esterified	3.5	0.8	29	55	4.3	7.0
2. Pulp storage tower						
Free	3.0	0.6	54	32	6.1	5.0
Esterified	4.3	0.6	24	55	9.0	7.0
3. Machine chest wall						
Free	4.7	1.4	59	28	3.0	4.5
Esterified	11.5	2.5	46	34	2.5	3.4
4. Broke chest wall						
Free	3.4	0.7	58	29	3.3	5.0
Esterified	5.5	1.4	27	55	3.5	8.2
5. Machine wire water pit						
Free	7.0	1.2	47	37	3.1	5.0
Esterified	13.0	4.0	54	24	2.6	2.4
6. Felt water pit						
Free	4.0	1.2	52	35	2.8	5.3
Esterified	6.0	2.6	37	42	5.6	6.1
7. Backwater race for feltwater						
Free	4.8	1.3	47	36	5.2	6.3
Esterified	5.5	1.2	21	60	3.4	9.0

[a] C_{16} = palmitic, C_{18} = stearic, C_{18}^1 = oleic, C_{18}^2 = linoleic, C_{18}^3 = linolenic, and C_{20} = a achidic acid.

An explanation for these anomalies will not be possible until the different classes of fatty esters in *P. radiata* wood have been fully characterized and their properties studied.

CONCLUSIONS

The results of this investigation show that screening is not a satisfactory method for the removal of resin from *P. radiata* bisulfite pulp. About 50% of the resin present in the wood was lost during the cooking process, an additional 11% by blowpit washing, and a further 8% by screening. The amount of resin removed by diffusion washing in the blowpits was not increased when the water temperature was raised from 145°F to 200°F. Resin acids and fatty acids were preferentially removed during washing and screening of the pulp, whereas the amounts of fatty acid esters were not significantly reduced.

Pitch deposits were mixtures of resin and inorganic material, and the trouble caused by a particular deposit was related to its viscosity. The resin contained about 50% acidic compounds. The fatty acid and unsaponifiable fractions showed the greatest tendency to accumulate in pitch deposits. Some pitch accumulations contained dihydroabietic acid, and the presence of this acid was related to the length of time which had elapsed after deposition of the pitch.

EXPERIMENTAL

Sample Preparation

Pinus radiata wood chips and bisulfite pulps were provided by Apcel Pty. Ltd., Millicent, South Australia. The chips were collected immediately before entry into the digester, and the time period between felling of the trees and pulping of the wood was about 3 weeks. Chips and pulp samples were stored at 4°C until analyzed. The chips were dried for 2 days on a freeze dryer, ground in a Wiley mill to pass a 40-mesh screen, and extracted with petroleum (b.p. 40–60°C) for 8 hr. Samples of pulp collected from the same digester cook, as it passed through the various stages in the pulp mill, were dried and extracted in a similar way. Matched samples of cooked and uncooked chips were obtained by taking a portion of a well-mixed chip sample and suspending it within a digester in a metal basket during a normal cooking cycle. The pitch samples were dried, extracted with acetone, and the insoluble portions collected by filtration. The filtrates were evaporated and the residual oils dried at 40°C under vacuum.

The acetone-soluble fractions of pitch were examined by using Method A, and the petroleum extracts from the chips and pulps analyzed by using Method B. Method A was used for extracts from unwashed pulp as they contained traces

of strong acid which interfered with the ion exchange column.

Analytical Procedures

Method A. To ensure quantitative results from this method it was essential that any emulsions were allowed to separate completely and that ethereal and aqueous phases were back-washed to eliminate losses of material. The sample was dissolved in acetone and the resin acids precipitated as their cyclohexylamine salts, which were collected by filtration and washed with petroleum. The combined acetone–petroleum filtrates were evaporated and the residue dissolved in ether. Excess cyclohexylamine was removed by washing the solution with 0.5N HCl and the fatty acids extracted with 3% NaOH. Evaporation of the ether and saponification of the neutral material with alcoholic KOH gave the esterified fatty acid and unsaponifiable fractions.

The resin acids were recovered by treatment of the cyclohexylamine salts with boric acid. The methyl esters of the resin and fatty acids were prepared by using excess ethereal diazomethane.

Method B. The relative amounts of resin acid, fatty acid, and esterified fatty acid fractions in the petroleum extract were determined by the method described in a previous paper (*16*). The unsaponifiable fraction was determined by Method A.

Spent Liquor

Extraction of spent liquor with ether gave 0.15% ether-soluble material, and a portion (1.5 g) was chromatographed on a column of silica gel. The fraction eluted with 5% ether–petroleum was chromatographed a second time by using the same solvent, and this procedure gave a mixture of phenolic compounds (0.5 g). This mixture consisted of eugenol and *trans-iso*-eugenol (GLC peak areas 2:1), which were separated by preparative GLC with a Versamide 900 column.

A second portion (1.5 g) of the ether extract was dissolved in acetone and the resin acids (0.61 g) precipitated as their cyclohexylamine salts.

Gas–Liquid Chromatography

Analytical GLC and analyses of the chromatograms were carried out as outlined in a previous paper (*16*). Preparative GLC was carried out with 15 ft, ⅜ in. OD glass columns packed with either 5% Versamide 900 on DMCS Chromosorb W or 5% diethylene glycol succinate on DMCS Chromosorb W.

Identification of Individual Fatty and Resin Acids

The methyl esters of fatty and resin acids were identified by comparison of

GLC retention times of known compounds with those of sample peaks on columns containing several different liquid phases. Samples of the methyl esters of pimaric, isopimaric, sandracopimaric, abietic, and dehydroabietic acids were collected by preparative GLC using a Versamide 900 column and their mass spectra compared to those published in the literature. Larger samples of methyl dehydroabietate, pimarate, and abietate were collected and their NMR spectra determined.

Methyl dihydroabietate was isolated by preparative GLC by using firstly a Versamide 900 column and then purifying the collected material with a diethylene glycol succinate column.

LITERATURE CITED

1. Cohen, W. E., "Influence of Resins on Paper Manufacture," *in* "Wood Extractives" (W. E. Hillis, Ed.), New York, Academic Press, 1962, Chap. 13, p. 421.
2. Nishida, K., Kuroki, K., and Ono, T., *J. Japanese Tech. Assoc. Pulp Paper Ind.* **13** (11): 800 (1959).
3. Malevskaya, S. S., Lyamtseva, Y. F., and Lyamtsev, D. Y., *Zh. Prikl. Khim.* **34** (11): 2533 (1961).
4. Malevskaya, S. S. and Litvinova, V. B., *Bumazh. Prom.* **39** (12): 7 (1964).
5. Kahila, S. K., *Paperi ja Puu* **46** (11): 615 (1964).
6. Talmud, S. L. and Ioffina, E. M., *Zh. Prikl. Khim.* **30** (6): 496 (1957).
7. Thommen, E. K., *Paper Trade J.* **136** (21): 17 (1953).
8. Kuroki, K., *Japan. Wood Res. Soc.* **3** (5): 161 (1957).
9. Swan, B., *Svensk Papperstid.* **71** (11): 436 (1968).
10. Nelson, P. F. and Kalkipsakis, C. G., *Holzforschung* **17** (5): 134 (1963).
11. Davies, G. W., *Svensk Papperstid.* **73** (24): 790 (1970).
12. Back, E. L., *Svensk Papperstid.* **72** (4): 109 (1969).
13. Hemingway, R. W. and Hillis, W. E., *Appita*, in press.
14. McDonald, I. R. C. and Porter, L. J., *New Zealand J. Sci.* **12** (2): 352 (1969).
15. Porter, L. J., *New Zealand J. Sci.* **12** (4): 687 (1969).
16. Hemingway, R. W., Nelson, P. J., and Hillis, W. E., *Tappi* **54** (1): 95 (1971).
17. Takeda, H., Schuller, W. H., and Lawrence, R. V., *J. Org. Chem.* **33** (4): 1683 (1968).
18. Takeda, H., Kanno, H., Schuller, W. H., and Lawrence, R. V., *I and EC Prod. Res. Dev.* **7** (3): 186 (1968).
19. Affleck, R. R. and Ryan, R. G., *Pulp Paper Mag. Can.* **70** (24): 107 (T563) (Dec. 19, 1969).
20. Glover, G. F. and Purdie, A. J. C., *Brit. Paper Board Makers' Assoc. Proc. Tech. Sect.* **38** (1): 1 (1957).
21. Starostenko, N. P., Nepenin, N. N., and Leshchenko, I. G., *Bumazh. Prom.* **32** (9): 2 (1957).
22. Back, E. L., *Svensk Papperstid.* **63** (17): 556 (1960).